SPOS vs. Laser Diffraction

AccuSizer® SPOS System

OVERVIEW

While laser diffraction is a popular particle size analysis technique for many reasons, no single method is perfect for every sample/application. This technical note describes how the single particle optical sizing technique may be a superior or complementary technique for customers only familiar with laser diffraction.

INTRODUCTION: SPOS

Single particle optical sizing (SPOS) is a common technique for measuring both the size and concentration of particles suspended in liquid.[1, 2, 3] In the SPOS technique, particles in liquid suspension flow through a photozone where they interact via extinction and/or scattering with a laser light source (Figure 1). The extinction/scattering by the particle is related to particle size and concentration through the use of a pulse height analyzer and a calibration curve. The result generated is the concentration and particle size distribution of the particles in suspension.

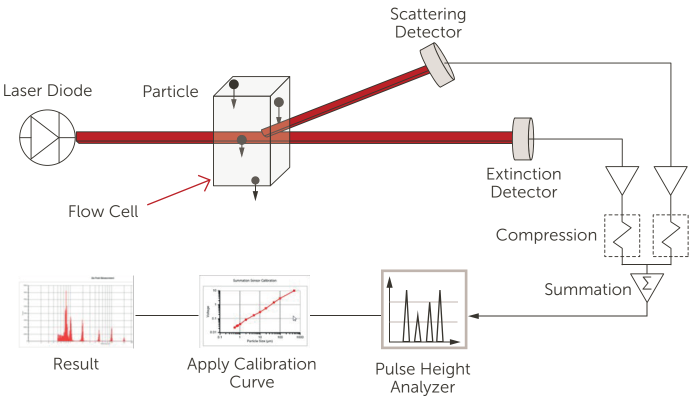


Figure 1. The LE400 SPOS sensor

As a particle passes through the photozone (sensing zone), light is either absorbed or refracted due to the physical presence of the particle or it can be scattered at some oblique angle. The magnitude of this pulse is dependent on the cross-sectional area of the particle and the physical principle of detection – either light scattering (LS) or light blocking. Light blockage is often referred to as light obscuration or light extinction (LE). Light obscuration allows for high resolution particle sizing and counting down to 1 micron.

Below 1 micron, light scattering is the necessary mode of detection wherein the light scattered by smaller submicron particles is detected and particle size is extracted. The SPOS technique used in the AccuSizer® line of instruments employs a patented LE and LS dual detection system that allows for single particle sizing and counting down to 0.5 microns (Figure 1). The illumination and detection system in the sensor is designed to provide a monotonic increase in pulse height with increasing particle diameter. As each successive particle passes through the sensor, a particle size distribution is created by comparing the detected pulse heights with a standard calibration curve, obtained from a set of uniform particles of known diameters.

The particle suspension must be sufficiently dilute so that the particles pass one at a time through the illuminated region, avoiding coincidences. This is accomplished by manual predilution or an automated dilution process. Various AccuSizer systems are designed to measure samples without dilution (AccuSizer SIS), with single stage exponential dilution (AccuSizer AD), or with two stage dilution (AccuSizer APS).

INTRODUCTION: LASER DIFFRACTION

The SPOS method is in stark contrast to the laser diffraction technique that measures all particles in the sample at the same time (Figure 2). Instruments that perform particle size analysis using ensemble techniques, such as laser diffraction, are inherently limited in accuracy and resolution since the raw detected signal is “inverted” mathematically in order to estimate the particle size distribution.

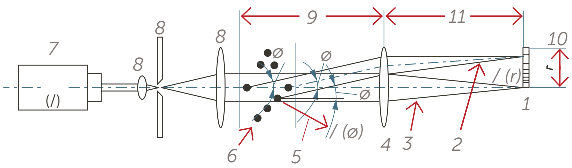


Figure 2. Laser diffraction optics [4]

Where:

1. Obscuration/optical concentration detector
2. Scattered beam
3. Direct beam
4. Fourier lens
5. Scattered light not collected by lens 4
6. Ensemble of dispersed particles
7. Light source (e.g.; laser)
8. Beam processing unit
9. Working distance of lens 4
10. Multi-element detector
11. Focal distance of lens 4

FACTORS EFFECTING LASER DIFFRACTION RESULTS

After the light scattering is collected on the multiple detectors in a laser diffraction system, an algorithm is used to convert scattered light to particle size. The calculated result is influenced by inter–connected factors including:

- Optical design
- Algorithm; Fraunhofer or Mie theory
- Refractive index of the sample/dispersing medium

International Journal of Pharmaceutics[5] explains the effect of optics and algorithm resulting from a laser diffraction analyzer with the PIDs detectors turned on and off and using Fraunhofer vs. Mie theory, see Figure 3.

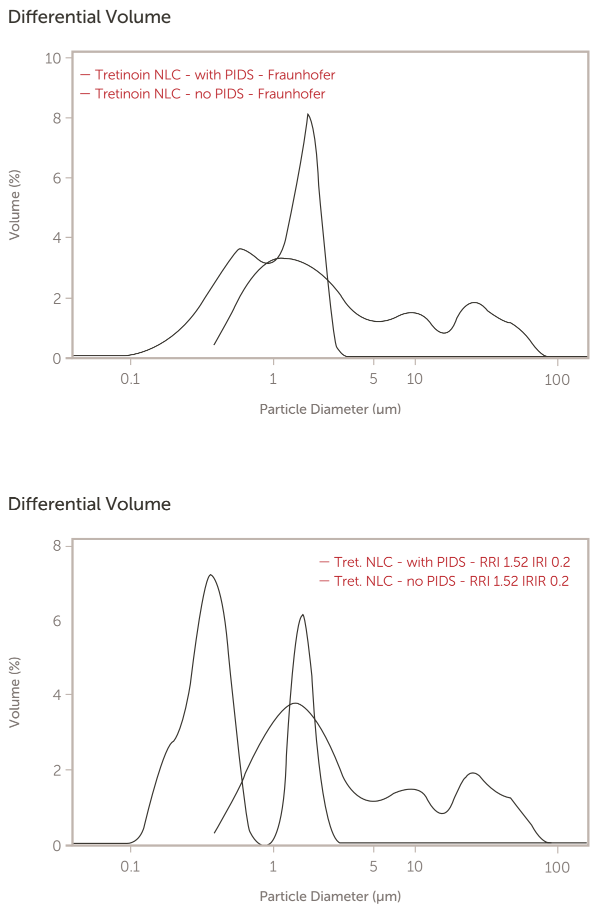


Figure 3. Effect of optics/algorithm

The same publication then presented six different calculated results from the same measurement to explain the effect of refractive index (RI) on results, see Figure 4.

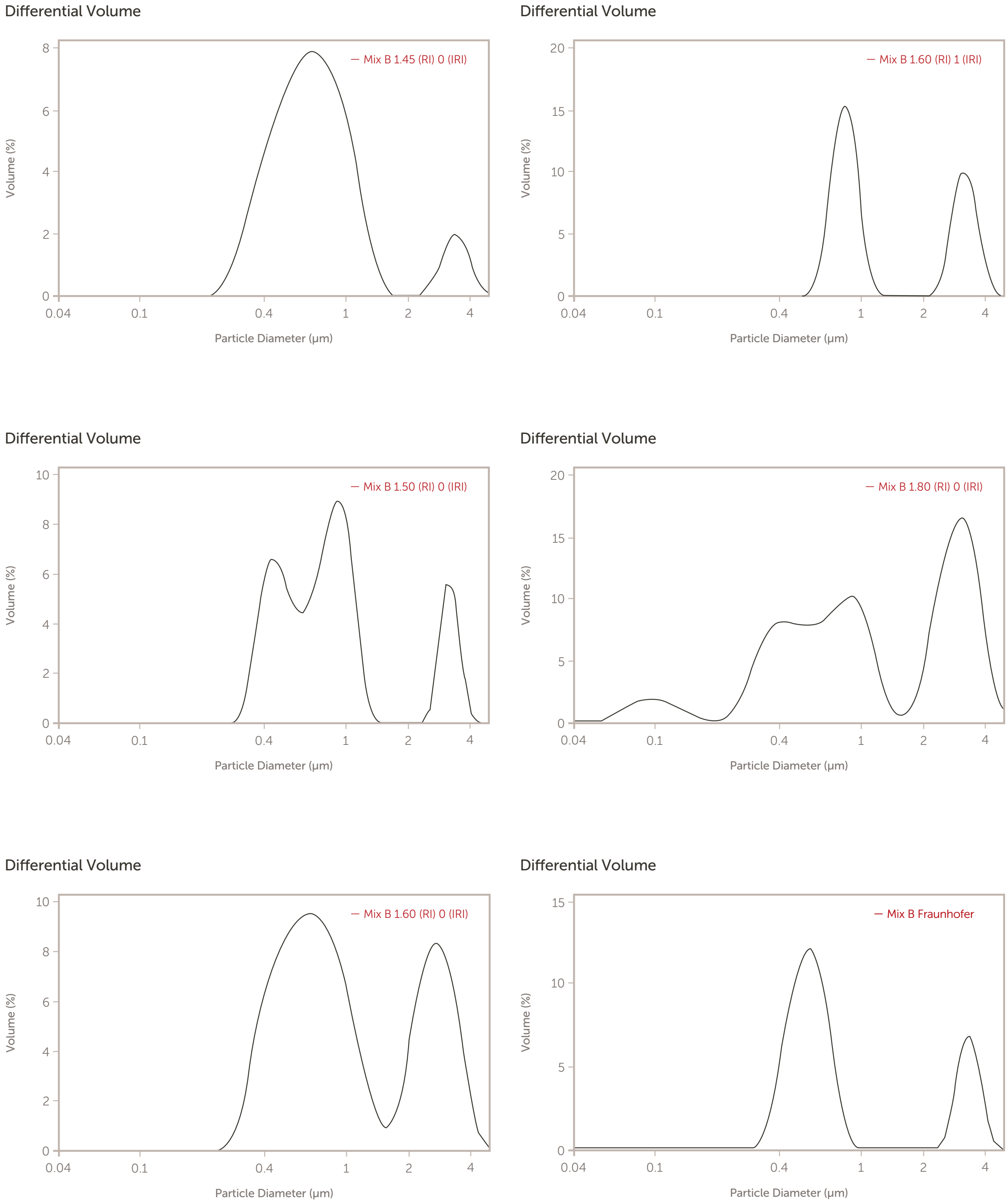


Figure 4. Effect of RI on calculated results

Looking at the wide variation in results depending on choice of RI it is easy to understand why some users express concern over the best approach to select RI for optimum results.

EXPERIMENTAL

A study was conducted using a popular laser diffraction analyzer, with all measurements made by an expert user (20+ years experience). The first sample was a silica based CMP slurry used in the microelectronics industry. The sample was analyzed once and then results were calculated using Fraunhofer (red) and Mie theory (green), see Figure 5.

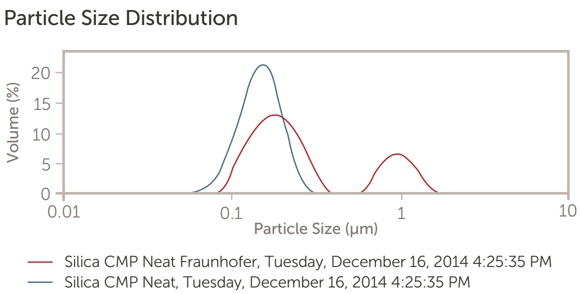


Figure 5. Fraunhofer vs. Mie results

The Fraunhofer result generates a ghost peak at 1 µm that does not actually exist. For this particular application customers are extremely focused on the presence of particles >1 µm, so misinterpreting this result would cause serious difficulties.

The laser diffraction analyzer manufacturer always suggests using Mie theory to generate better results – but what RI value to use? Ideally, the RI of the sample can either be measured or found through references. This often works well and generates acceptable results. But for samples where it is impossible to determine the optimum RI, choice users are instructed to refer to an error calculation known as the Residual as the proper way to select the best RI value. The RI choice that minimizes the Residual should hopefully generate the best result.

This approach of basing the RI selection on the lowest Residual value was tested using an Al based CMP slurry spiked with 1 µm PSL particles. A peak at 1 µm should be found in the result using this sample. The results from the laser diffraction analyzer are shown in Figure 6. The green result used RI values 1.78, 0.1 and the red result used RI values 1.59,0.

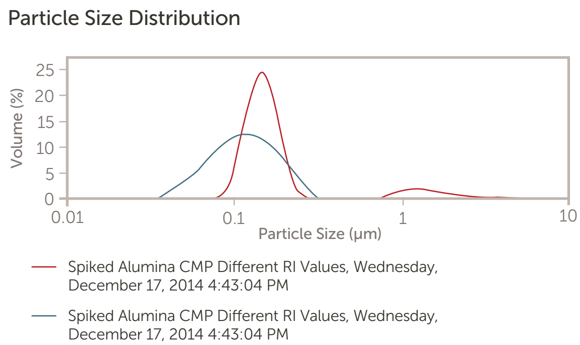


Figure 6. Al CMP slurry spiked with 1 µm PSL

The calculated results from this measurement are shown in Figure 7.

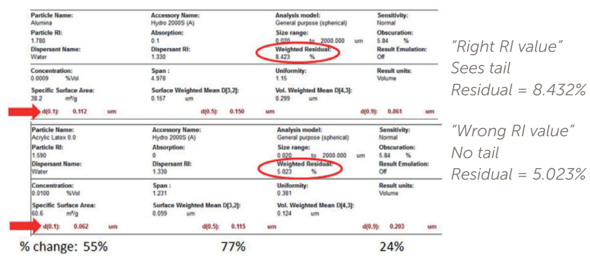


Figure 7. Calculated results for spiked Al CMP slurry

The RI choice (1.78, 0.1) found the 1 µm spike peak, but had a higher Residual value (8.423%) than the choice (1.59, 0.0) that missed the spike peak (5.023%).

This example attempts to portray the challenge in using the laser diffraction technique. The algorithm and RI choice are critical and greatly effect the final result. But choosing the RI value and validating the choice by using the Residual calculation is not always a straight forward approach.

SENSITIVITY TO TAILS OF DISTRIBUTIONS

Any technique that measures particles one at a time, such as the SPOS, is inherently higher resolution than an ensemble light scattering technique, such as laser diffraction. Theoretically, if there is one particle in a swimming pool and the entire volume is passed through an SPOS sensor, the system will find and measure the one particle. Laser diffraction would never find this particle. The next set of experiments was performed to compare the two techniques with respect to sensitivity to a known tail of particles larger than the main peak.

ACCUSIZER RESULT

To test the SPOS technique 3.4 µL of 1 µm PSL particles were added to 250 mL of silica based CMP slurry. This sample was measured on the AccuSizer Mini FX system and the result is shown in Figure 8. Not only was the peak detected, but the increase in concentration closely matched the expected value.[6]

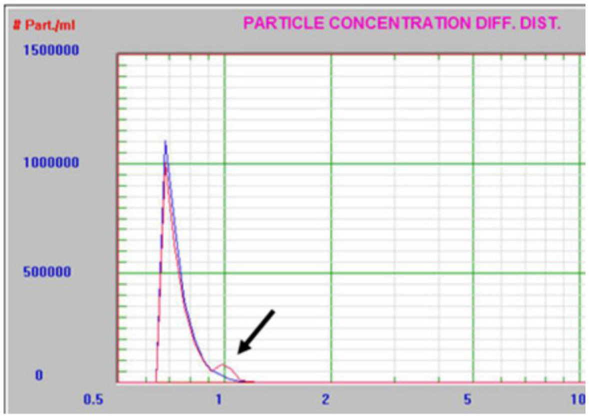


Figure 8. AccuSizer SPOS result of spiked silica CMP slurry

LASER DIFFRACTION RESULT

The same silica based CMP slurry and 1 µm PSL particles were mixed to determine what concentration was required for the laser diffraction analyzer to first report the presence of the tail distribution. After adding 177 µL of the PSL particles to 250 mL of the CMP slurry, no tail had yet to appear (see Figure 9).

Particle Size Distribution

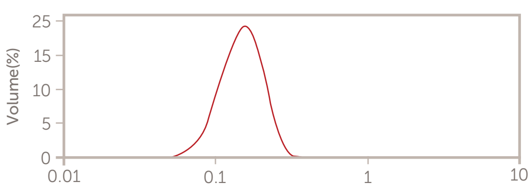


Figure 9. Laser diffraction result, 177 µL PSL into 250 mL silica CMP slurry

After it became apparent that a large volume of PSL particles would be required to find the spike peak, the base CMP volume was drastically reduced to ~4 mL. The PSL peak was finally reported after 360 µL of was added to 4.3 mL of the base silica CMP slurry. This result is shown in Figure 10.

Particle Size Distribution

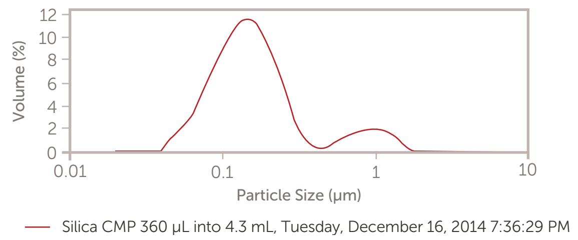


Figure 10. Laser diffraction result; 360 µL into 4.3 mL silica CMP slurry

Comparing the two techniques, this experiment suggests that the AccuSizer SPOS system is over 600 times more sensitive to the present of a tail distribution than the laser diffraction technique.

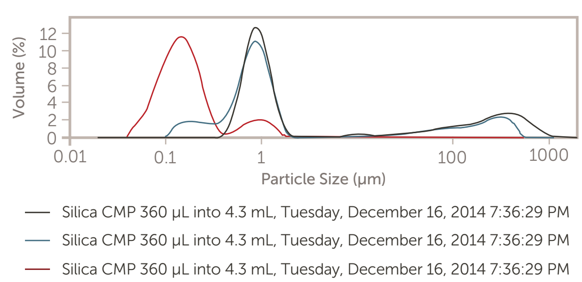
CONCENTRATION CALCULATIONS

0.0034/250	=	.0000136
0.36/4.3	=	0.0837
0.0837/.000136	=	615.44

EFFECT OF RI (AGAIN)

The result shown in Figure 10 was then recalculated to again test the approach to use the lowest Residual value as a valid approach to determine optimum RI values. The results from three calculations are shown in Figure 11.

Particle Size Distribution



RI	Residual	1st peak	2nd peak
Right	6.027%	0.14 µm	1.1 µm
Wrong 1	2.137%	1.10 µm	316 µm
Wrong 2	1.359%	0.95 µm	364 µm

Figure 11. Calculated results for spiked silica CMP slurry

The relationship between residual and accuracy of result is directly inverse of the expected trend; the highest residual gave the best result.

SPREADING OF DISTRIBUTION

Another approach to define technique resolution is to determine how much the calculated result is broader than the expected value. The broader the result spreads – the lower resolution the technique. To investigate this attribute of the two techniques, a sample that passed through a 45 µm sieve was analyzed on a laser diffraction analyzer and the AccuSizer. These results are shown in Figure 12. The AccuSizer results in blue clearly shows the truncated distribution while the laser diffraction results in red broadens the distribution to include particles >100 µm that do not exist.

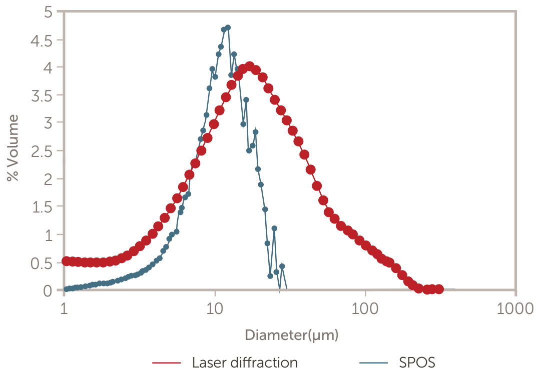


Figure 12. SPOS vs. laser diffraction results for a sieved sample

CONCLUSIONS

The SPOS technique incorporated in all AccuSizer systems is a high resolution and high accuracy technique that provides both particle size and concentration results. The resolution and sensitivity to distribution tails is far superior to laser diffraction.

References

[1] Kissa, E., (1999), Dispersions: Characterization, Testing, and Measurement, New York, NY: Marcel Dekker, 1999

[2] White, D., PSD measurement using the single particle optical sizing (SPOS) method, Géotechnique, Volume 53, Issue 3, 01 April 2003 , pages 317 –326

[3] Barany, S. et. al., PSD measurement using the single particle optical sizing (SPOS) method, Colloids and Sur-faces, Volume 106, Issues 2–3, 22 January 1996, Pages 213–221

[4] ISO 13320, Particle size analysis—Laser diffraction methods

[5] Keck and Muller, Size analysis of submicron particles by laser diffractometry—90% of the published measurements are false, International Journal of Pharmaceutics 355 (2008) 150–163

[6] Entegris Application Note Detecting Tails in CMP Slurries.

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